



Cathode Process at the Electrolysis of $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ Melts and Suspensions

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The kinetics of the cathode process on tungsten in $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ melts and suspensions was studied by means of voltammetry and galvanostatic polarization. The effects of the temperature, $[\text{KF}]/[\text{AlF}_3]$ ratio, Al_2O_3 content on the kinetic parameters of electrowinning of aluminum from the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ melts and suspensions were determined. Introducing Al_2O_3 slurry into the suspension and increasing its proportion make the diffusion of the electroactive ions to the cathode more difficult. The parameters for the suspension electrolysis were chosen on the basis of electrochemical measurements. The possibility of aluminum production during the electrolysis of $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ suspension with 45 wt% Al_2O_3 in the solid phase was demonstrated.

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The electrolytic production of aluminum from low-temperature melts and suspensions is a very promising technique.^{1–5} New electrode and construction materials can be used to permit a lowering of the electrolysis temperature by 150–200°C.^{6–11} This also serves to increase the average life of the electrolytic cell. Usage of suspensions with solid particles of Al_2O_3 allows the maximum concentration of the electroactive ions to be maintained near the electrodes at the working temperature during the electrolysis.

The Al_2O_3 content in the electrolytes of industrial electrolytic cells varies in the range of 2–4 wt%, whereas its solubility is about 8 wt%.^{12–14} The low Al_2O_3 content is mainly caused by the rapid phase transformation $\gamma\text{-Al}_2\text{O}_3 \rightarrow \alpha\text{-Al}_2\text{O}_3$ at temperatures above 850°C.^{15–17} The latter form of alumina ($\alpha\text{-Al}_2\text{O}_3$) dissolves in a cryolite-alumina melt much more slowly than the former. Thus, an excess of Al_2O_3 promotes the formation of crusts at the bottom of the electrolyzer. The lowering of the temperature reduces the rate of $\alpha\text{-Al}_2\text{O}_3$ formation and allows melts saturated with Al_2O_3 to be used as well as the suspensions.^{1–5} In this case, the rate of the electrochemical process (current density) is likely to be solely due to the Al_2O_3 dissolution.

In terms of the anode process, the using $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ suspension for the electrolytic production of aluminum at lower temperature can reduce the chemical oxidation of carbon anodes and provide faster removal of anode gases from the denser electrolyte.

The present work is devoted to a determination of the kinetic features of the cathode process on tungsten in $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ melts and suspensions. The KF-AlF_3 -based molten systems were chosen due to the higher solubility of Al_2O_3 at the investigated temperatures with other conditions remaining constant.^{18–20} The results of the study supplement scarce data on the kinetics of aluminum electrowinning from $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ melts and suspensions.^{21–23}

Experimental

Preparation of electrolytes.—The melts and suspensions were prepared from individual KF , AlF_3 (Chemically Pure Grade, OJSC “Vekton”, Russia) and Al_2O_3 (UC “RUSAL”) compounds. The mixture of KF and AlF_3 having the required $[\text{KF}]/[\text{AlF}_3]$ ratio was placed into the corundum crucible of the electrochemical cell and heated up to the working temperature by means of a resistance furnace. Then the prepared KF-AlF_3 mixtures were purified by means of potentiostatic electrolysis to remove residuals (electropositive in relation to

the aluminum impurities; 2 hours at a 0.2 V vs. the potential of aluminum electrode²⁴). Aluminium oxide was added into the purified KF-AlF_3 melts. Data on Al_2O_3 solubility in the investigated melts and suspensions at the temperatures under study are presented in Table I. Suspensions having a 30% and 45% excess of alumina were chosen for experimental purposes based on the sedimentation effect: the study of cathode processes having a lower solid phase content is complicated by rapid sedimentation.

Electrochemical measurements.—Electrochemical measurements were carried out at temperatures of 670–800°C in a three-electrode corundum cell under air. Tungsten (W) rods (1 mm, immersion 10 mm) served as a working electrode. A graphite cylinder was used to form a counter electrode (working surface 12 cm²). The potential of the working electrode was measured relative to the potential of the aluminum reference electrode.²⁴

AutoLab 320N and NOVA 1.11 potentiostat/galvanostat software solutions (Metrohm, Netherlands) were used. The voltammograms were recorded at potential sweep rates from 0.01 to 0.5 V s^{−1}. Galvanostatic polarization curves were obtained by the fixation of the stationary potential at different cathode current impulses. In order to compensate the circuit resistance, both FRA and I-Interrupt procedures were used. The temperature was controlled and kept within ±2°C by a Varta TP703 thermal regulator calibrated with a chromel–alumel thermocouple and a USB-TC01 thermocouple module (National Instruments, USA).

Electrolysis test.—Electrolysis of the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ suspension was performed at 715°C in a corundum electrolytic cell under air. A vertical electrode arrangement was used. A tungsten plate (surface 2 × 50 cm²), placed at the center of the corundum crucible with the $\text{KF-AlF}_3\text{-Al}_2\text{O}_3$ suspension, served as a cathode. Two graphite anodes (plates with the front surface of 25 cm²) were located near the crucible wall. The anode-cathode distance was 2 cm. Al_2O_3 was added to the electrolytic cell following the immersion of the electrodes. The voltage between the cathode and anodes was recorded during the electrolysis.

Results and Discussion

Voltammetry.—The typical cyclic voltammograms (CVs) obtained on W electrode in 1.5 $\text{KF-AlF}_3\text{-Al}_2\text{O}_3(\text{sat})$ melt are shown on Fig. 1. The temperatures were 715, 750, and 800°C and the potential sweep rate (v) varies from 0.01 to 0.5 V s^{−1}. CVs contains one cathode peak (Al) of the aluminum reduction at −0.2...−0.3 V (vs. Al) and a wave

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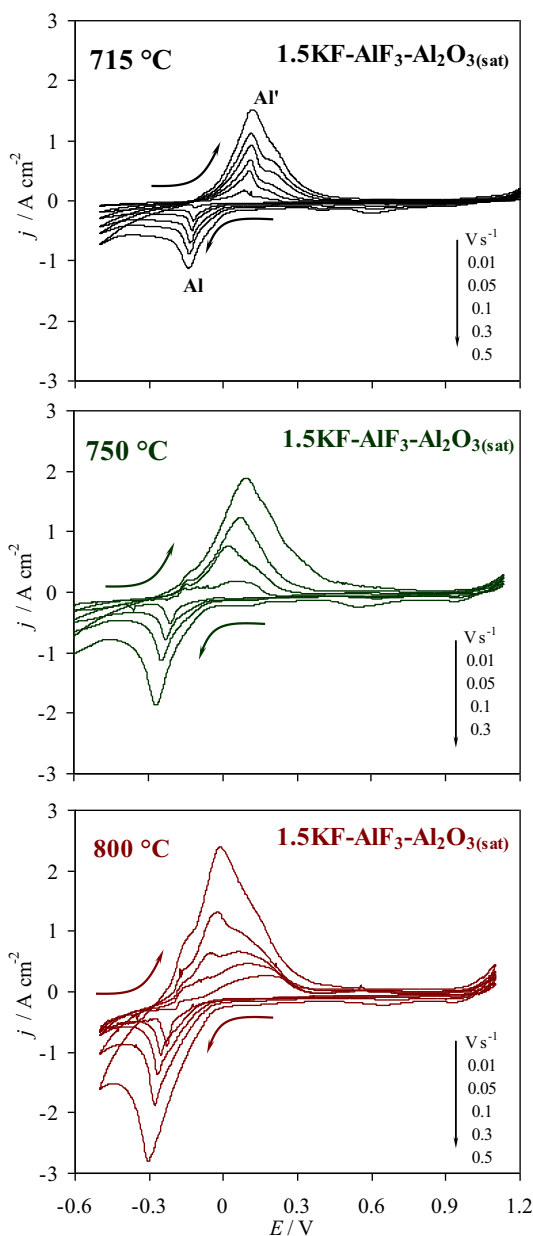
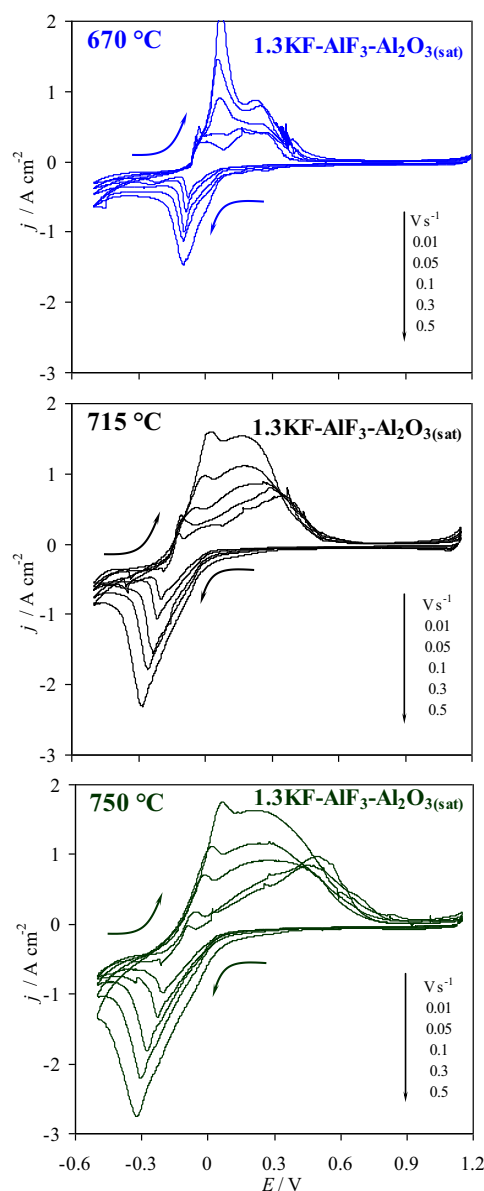
Table I. Al_2O_3 solubility in the melts under study.

Melt/suspension composition, wt %	$[\text{KF}]/[\text{AlF}_3]$, Mol mol ⁻¹	Electrolyte	Al_2O_3 solubility (wt%) at the T , °C ^{18–20}			
			670	715	750	800
47.4KF-52.6AlF ₃	1.3	1.3KF-AlF ₃ -Al ₂ O _{3(sat)}	4.20	4.85	5.50	
50.9KF-49.1AlF ₃	1.5	1.5KF-AlF ₃ -Al ₂ O _{3(sat)}		5.70	6.85	8.35

of the potassium reduction (**K**) at more negatively values than -0.5 V (vs. Al). There is one peak (**Al'**) of aluminum oxidation on the anode sides of CVs at $0.1 \dots 0.2$ V (vs. Al). The complicated form of anode peak can indicate different forms of reduced aluminum.²³ The rise of the working temperature from 715 to 800°C multiplies the values of the anode and cathode currents on CVs by 1.5–2.0. At the same time the peak currents on CVs at 750 and 800°C are closely matched. We assume that this is due to the reducing diffusion resistances with

increasing temperature. Analogous CVs were obtained in the 1.3KF-AlF₃-Al₂O_{3(sat)} melt (Fig. 2).

The effects of the 30 and 45 wt% solid Al_2O_3 additions to the KF-AlF₃-Al₂O_{3(sat)} melts on CVs at different temperatures (for $\nu = 0.1 \text{ V s}^{-1}$) are shown in Figs. 3 and 4. As is seen, the addition of the solid Al_2O_3 and further increases of its content in the KF-AlF₃-Al₂O_{3(sat)} suspensions decrease the peak current densities (j_{pc}) of the aluminum electrowinning (especially at the higher temperatures of 750 and 800°C).

**Figure 1.** CVs obtained on W electrode in 1.5KF-AlF₃-Al₂O_{3(sat)} melt at different temperatures. Potential sweep rates -0.01 – 0.5 V s^{-1} .**Figure 2.** CVs obtained on W electrode in 1.3KF-AlF₃-Al₂O_{3(sat)} melt at different temperatures. Potential sweep rates -0.01 – 0.5 V s^{-1} .

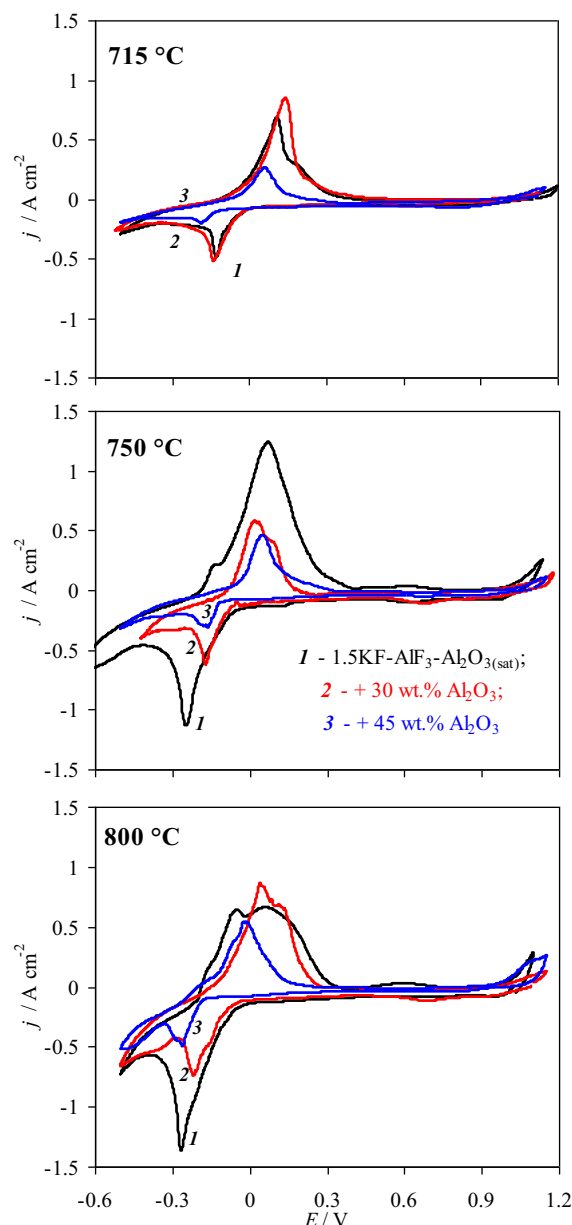


Figure 3. CVs obtained on W electrode in 1.5KF-AlF₃-Al₂O₃ melt (I) and suspensions with 30 (2) and 45 (3) wt% of the solid Al₂O₃ at different temperatures. Potential sweep rate -0.1 V s^{-1} .

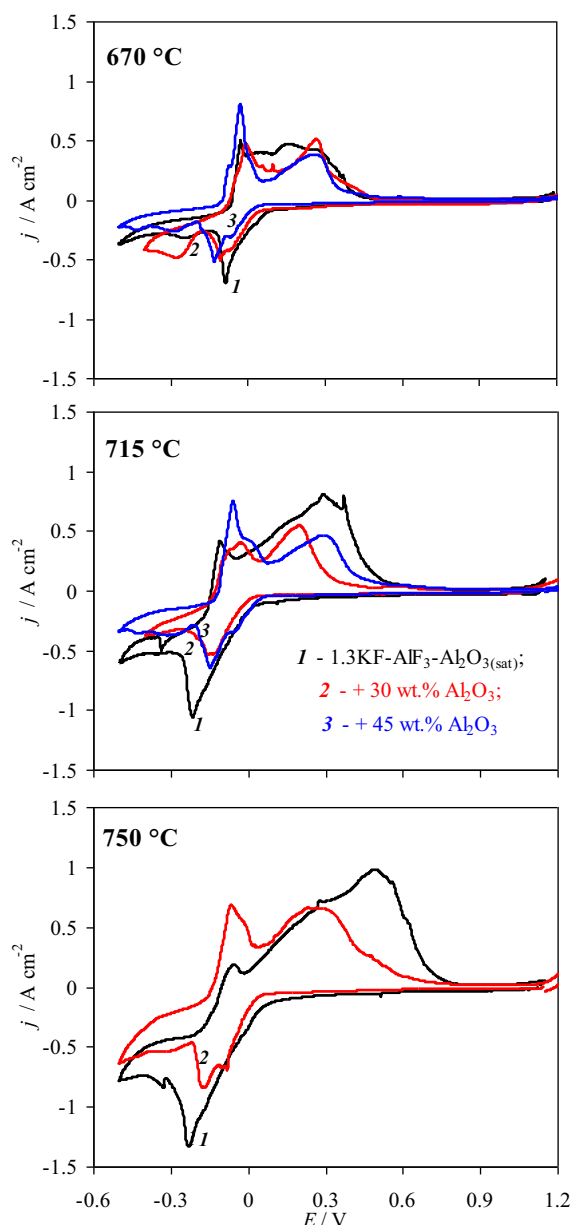


Figure 4. CVs obtained on W electrode in 1.3KF-AlF₃-Al₂O₃ melt (I) and suspensions with 30 (2) and 45 (3) wt% of the solid Al₂O₃ at different temperatures. Potential sweep rate -0.1 V s^{-1} .

The values of potentials (E_{pc}) and cathode peak current densities (j_{pc}) at different temperatures (T) and potential sweep rates (v) for the aluminum electrowinning from the KF-AlF₃-Al₂O₃ melts and suspensions are listed in Tables II and III. Relationships $j_{pc}(v^{1/2})$ for all conditions are generally linear (Fig. 5). This means that the process under study is primarily limited by the diffusion. Some shifting of E_{pc} with the v rising indicates the quasi-reversibility of the process (Tables II and III). Conversely, the increases in the solid Al₂O₃ content in the KF-AlF₃-Al₂O_{3(sat)} suspensions made the diffusion more difficult. Numerically, the described effects can be analyzed from the diffusion coefficients (Table IV) of the electroactive ions (D) to the W electrode, estimated for the diffusion-controlled process by the Randles-Sevcik equation:^{25,26}

$$j_{pc} = -0.4463(zF)^{3/2}C(vD/RT)^{1/2}$$

where R – gas constant, $R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$; T – temperature, K; z – number of electrons, $z = 3$; F – Faraday constant, F

$= 96487 \text{ C mol}^{-1}$; j_{pc} – cathode peak current density, A cm^{-2} ; C – concentration of the electroactive ions, mol cm^{-3} ; v – potential sweep rate, V s^{-1} ; D – diffusion coefficient of the electroactive ions, $\text{cm}^2 \text{ s}^{-1}$.

Concentration C was calculated using the data both on the Al₂O₃ solubility in the KF-AlF₃-Al₂O₃ melts^{18–20} and the melt densities^{27,28} by equation $C = \rho\varphi/M_{\text{Al}_2\text{O}_3}$ (ρ – melt density, g cm^{-3} , φ – solubility of Al₂O₃, wt%, $M_{\text{Al}_2\text{O}_3}$ – molar mass of Al₂O₃, $M_{\text{Al}_2\text{O}_3} = 102 \text{ g mol}^{-1}$). The C values for the KF-AlF₃-Al₂O_{3(sat)} melts were taken for the D estimation in suspensions.

The D values in the KF-AlF₃-Al₂O₃ melts were from 0.5 to $3.4 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ depending on the temperature and $[\text{KF}]/[\text{AlF}_3]$ ratio (Table IV). These are close to the D values obtained for graphite and platinum electrodes in previous works.^{21,22} The addition of the solid Al₂O₃ and increases in its content in the KF-AlF₃-Al₂O_{3(sat)} suspensions lead to decreasing D values at the same temperature.

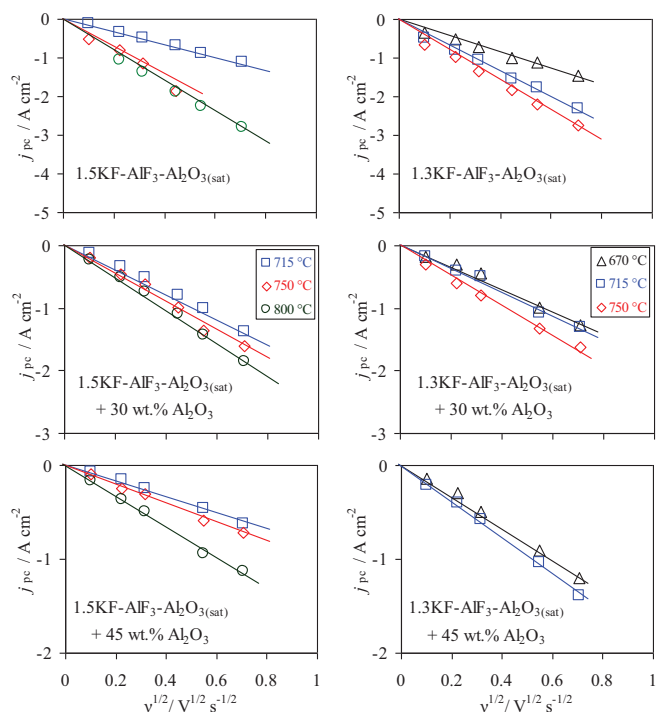


Figure 5. Relationships $j_{pc}(v^{1/2})$ for the aluminum electrowinning from KF-AlF₃-Al₂O₃ melts and suspensions at different temperatures.

Galvanostatic polarization.—The kinetics of stationary cathode processes on the W electrode in the KF-AlF₃-Al₂O_{3(sat)} melts and suspensions were investigated in order to determinate the suspension electrolysis parameters. Typical galvanostatic polarization curves (GPCs) – dependences of the W cathode potential on applied cathode current density at the electrowinning of aluminum from the KF-AlF₃-Al₂O_{3(sat)} melts – are shown on Fig. 6. Different temperatures and [KF]/[AlF₃] ratios were used. As is seen here, aluminum electroreduction taking place at the potentials more negative than 0 V with limit cathode current densities (j_d) achieved at $-0.2 \dots -0.4$ V (vs. Al). The values of j_d were from 0.15 to 0.70 A cm⁻² depending on the temperature and [KF]/[AlF₃] ratio in the melt. The considerable

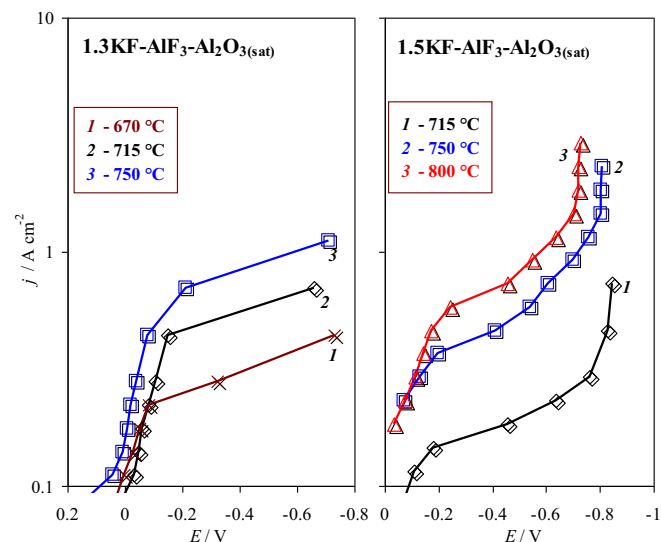


Figure 6. GPCs obtained on W electrode in KF-AlF₃-Al₂O_{3(sat)} melts at different temperatures.

increases in the current density at -0.7 – -0.8 V (vs. Al) on GPCs for the 1.5KF-AlF₃-Al₂O_{3(sat)} melt indicates potassium electroreduction. The temperature rises and lowering of [KF]/[AlF₃] ratios leads to increases in the j_d values.

The effects of the 30 and 45 wt% solid Al₂O₃ additions to the KF-AlF₃-Al₂O_{3(sat)} melts on GPCs signals at the different temperatures are shown on Figs. 7 and 8. As well as for CVs, the addition of the solid Al₂O₃ and further increases in its content in the KF-AlF₃-Al₂O_{3(sat)} suspensions decrease the j_d of the aluminum electrowinning for all temperatures. Decreases in the values of j_{pc} , D , and j_d (from CVs and GPCs) can be caused both by increasing the diffusion layer thickness (δ) and decreasing the convection flows with the addition of the solid Al₂O₃ phase.

Electrolysis test.—The parameters of the suspension electrolysis were determined on the basis of stationary measurements. The explanation of this choice is given below.

1. The suspension with the [KF]/[AlF₃] of 1.3 mol mol⁻¹ was chosen due to the lower liquidus temperature^{19,29} and larger limit current densities at the same other conditions. Hence, it is possible to carry out high-dissolution-rate electrolysis of Al₂O₃ at lower temperatures.¹⁹ Further lowering of the [KF]/[AlF₃] ratio can additionally decrease the possible operating temperature. However, this seems not to be appropriate due to the significant lowering of the Al₂O₃ solubility and its dissolution rate^{19,20} with temperature decreases. In addition, increases in the melt viscosity and the phase overvoltage should be taken into account.
2. The optimal temperature of the 1.3KF-AlF₃-Al₂O_{3(sat)} suspension electrolysis is 700–720°C. This temperature supports the liquid state of aluminum in the electrolytic cell and the lower electrolyte overheating.
3. The optimal content of solid Al₂O₃ in suspension is 45 wt%. Limit current densities for 1.3KF-AlF₃-Al₂O₃ suspensions with both 30% and 45 wt% Al₂O₃ are practically equal. At the same time, the sedimentation ability of the latter is lower. This is conducive for better separation of the anolyte and catholyte.

Electrolysis of the 1.3KF-AlF₃-Al₂O₃ suspension with 45 wt% Al₂O₃ in solid phase was carried out using the parameters:

current – 20 A;
cathode current density – 0.2 A cm⁻²;
anode current density – 0.4 A cm⁻²;
anode-cathode distance – 2 cm;
voltage – 4.5–6.0 V;
temperature – 715°C.

Photographs of the working electrolyzer as well as photos of the electrodes and solidified suspension after the electrolysis are presented in Fig. 9. Considerable gas evolution was observed on the anodes (including lateral sides) during the electrolysis (Fig. 9a). Composition of the anode gas was not determined in present work, but we assume that the CO₂ was the main anode product at a relatively high anode current density (more than 0.05–0.10 A cm⁻²).^{12,30,31} Cathodic aluminum was formed near the W cathode in form of 2–8 mm droplets (Fig. 9e). The cathode was also well wetted by aluminum (Fig. 9b). Cathode current efficiency (applied quantity of electricity–48 A · h) was above than 50%. This value is comparable to the cathode current efficiencies obtained for other types of laboratory electrolyzers.^{5,7,10}

The results obtained indicate the possibility of the electrolytic production of aluminum during the electrolysis of the low-temperature KF-AlF₃-Al₂O₃ suspension with relatively high current efficiency. However, further study is needed, including research into the processes (particularly the kinetics of the anode process as well as the composition of anode gases) during electrolysis and optimization of the suspension composition and electrolysis parameters.

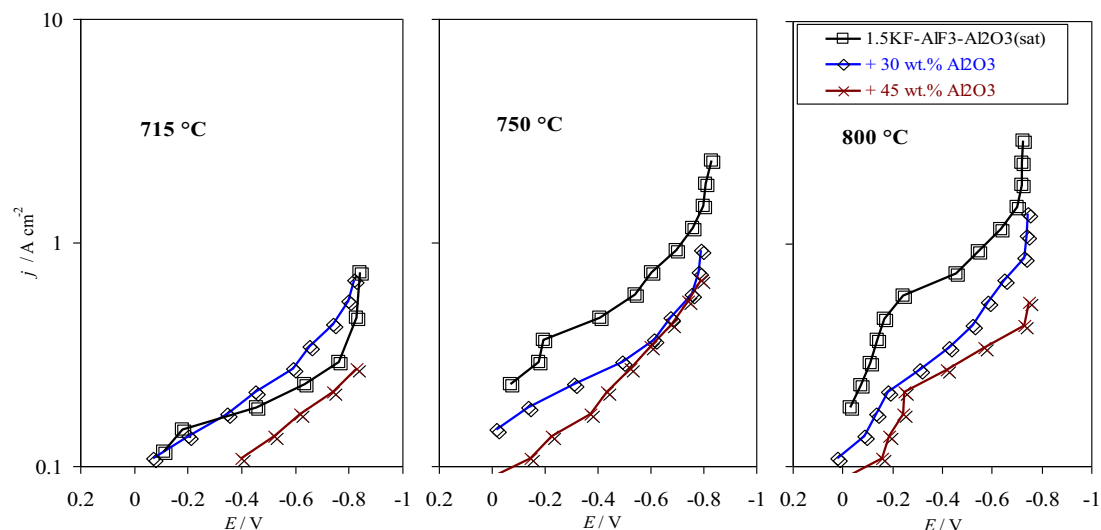


Figure 7. GPCs obtained on W electrode in 1.5KF-AlF₃-Al₂O_{3(sat)} melts and suspensions with 30 and 45 wt% of the solid Al₂O₃ at different temperatures.

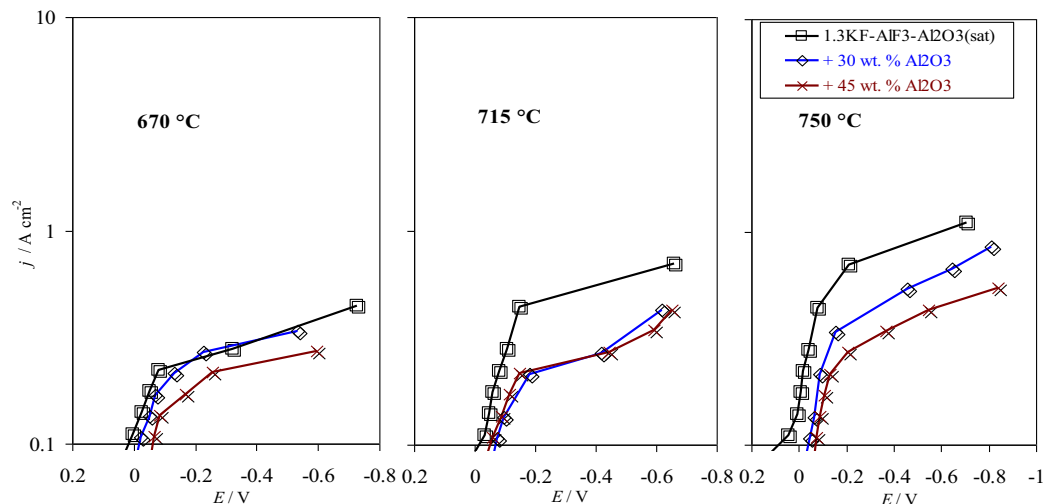


Figure 8. GPCs obtained on W electrode in 1.3KF-AlF₃-Al₂O_{3(sat)} melts and suspensions with 30 and 45 wt% of the solid Al₂O₃ at different temperatures.

Table II. Kinetic parameters of the aluminum electroreduction from 1.5KF-AlF₃-Al₂O₃ melt and suspensions.

$v/V \text{ s}^{-1}$	$v^{1/2}/V^{1/2} \text{ s}^{-1/2}$	715°C		750°C		800°C	
		E_{pc}/V	$i_{pc}/A \text{ cm}^{-2}$	E_{pc}/V	$i_{pc}/A \text{ cm}^{-2}$	E_{pc}/V	$i_{pc}/A \text{ cm}^{-2}$
		1.5KF-AlF ₃ -Al ₂ O _{3(sat)}					
0.01	0.1	−0.116	−0.12	−0.211	−0.52	−0.227	−0.89
0.05	0.224	−0.123	−0.33	−0.229	−0.79	−0.255	−1.06
0.1	0.316	−0.128	−0.49	−0.245	−1.13	−0.264	−1.36
0.3	0.548	−0.138	−0.87	−0.268	−1.87	−0.290	−2.27
0.5	0.707	−0.145	−1.12	—	—	−0.303	−2.80
		1.5KF-AlF ₃ -Al ₂ O _{3(sat)} ± 30 wt% Al ₂ O ₃					
0.01	0.1	−0.104	−0.12	−0.161	−0.19	−0.201	−0.23
0.05	0.224	−0.119	−0.34	−0.167	−0.46	−0.211	−0.50
0.1	0.316	−0.137	−0.52	−0.17	−0.63	−0.218	−0.74
0.3	0.548	−0.155	−1.01	−0.18	−1.37	−0.235	−1.43
0.5	0.707	−0.165	−1.37	−0.18	−1.61	−0.245	−1.85
		1.5KF-AlF ₃ -Al ₂ O _{3(sat)} ± 45 wt% Al ₂ O ₃					
0.01	0.1	−0.171	−0.07	−0.168	−0.09	−0.248	−0.16
0.05	0.224	−0.181	−0.15	−0.176	−0.25	−0.264	−0.37
0.1	0.316	−0.186	−0.24	−0.16	−0.31	−0.26	−0.49
0.3	0.548	−0.183	−0.43	−0.206	−0.59	−0.279	−0.94
0.5	0.707	−0.186	−0.63	−0.228	−0.72	−0.309	−1.13



Figure 9. Photos: *a* – working electrolyzer, *b* – W cathode, *c* – graphite anodes, *d* – solidified suspension, and *e* – cathode aluminum. Photos *b-e* – after the electrolysis of 1.3KF-AlF₃-Al₂O_{3(sat)} suspension with 45 wt% of the solid Al₂O₃ at 715°C.

Table III. Kinetic parameters of the aluminum electroreduction from 1.3KF-AlF₃-Al₂O₃ melt and suspensions.

$v/V \text{ s}^{-1}$	$v^{1/2}/V^{1/2} \text{ s}^{-1/2}$	670°C		715°C		750°C	
		E_{pc}/V	$i_{pc}/A \text{ cm}^{-2}$	E_{pc}/V	$i_{pc}/A \text{ cm}^{-2}$	E_{pc}/V	$i_{pc}/A \text{ cm}^{-2}$
		1.3KF-AlF ₃ -Al ₂ O _{3(sat)}					
0.01	0.1	−0.073	−0.35	−0.176	−0.49	−0.176	−0.67
0.05	0.224	−0.075	−0.52	−0.198	−0.79	−0.203	−0.98
0.1	0.316	−0.085	−0.71	−0.215	−1.06	−0.227	−1.33
0.3	0.548	−0.097	−1.13	−0.259	−1.78	−0.303	−2.21
0.5	0.707	−0.095	−1.46	−0.281	−2.31	−0.322	−2.75
		1.3KF-AlF ₃ -Al ₂ O _{3(sat)} ± 30 wt% Al ₂ O ₃					
0.01	0.1	−0.094	−0.17	−0.155	−0.18	−0.151	−0.30
0.05	0.224	−0.097	−0.30	−0.162	−0.41	−0.178	−0.60
0.1	0.316	−0.112	−0.44	−0.165	−0.50	−0.185	−0.80
0.3	0.548	−0.127	−0.99	−0.168	−1.08	−0.190	−1.32
0.5	0.707	−0.141	−1.27	−0.178	−1.30	−0.191	−1.62
		1.3KF-AlF ₃ -Al ₂ O _{3(sat)} ± 45 wt% Al ₂ O ₃					
0.01	0.1	−0.112	−0.14	−0.143	−0.21	—	—
0.05	0.224	−0.124	−0.29	−0.141	−0.40	—	—
0.1	0.316	−0.134	−0.49	−0.158	−0.58	—	—
0.3	0.548	−0.144	−0.91	−0.161	−1.03	—	—
0.5	0.707	−0.153	−1.20	−0.166	−1.39	—	—

Table IV. Diffusion coefficients ($D \times 10^5 / \text{cm}^2 \text{ s}^{-1}$) of electroactive ions in KF-AlF₃-Al₂O₃ melts and suspensions.

Melt	Excess of Al ₂ O ₃ , wt%	$T, ^\circ\text{C}$			
		670	715	750	800
1.5KF-AlF ₃ -Al ₂ O _{3(sat)}	0	—	0.5–0.6	2.9–3.0	3.2–3.6
	30	—	0.3–0.5	0.9–1.1	1.1–1.4
	45	—	0.1–0.3	0.3–0.4	0.6–0.8
1.3KF-AlF ₃ -Al ₂ O _{3(sat)}	0	2.2–2.6	4.6–5.0	5.4–6.2	—
	30	0.9–1.5	1.3–1.7	1.9–2.5	—
	45	0.8–1.3	1.4–1.5	—	—

Conclusions

The effects of the temperature, $[KF]/[AlF_3]$ ratio, Al_2O_3 content (melt, saturated with Al_2O_3 ; suspensions with 30 and 45 wt% Al_2O_3) on the kinetic parameters of the aluminum electrowinning from the $KF-AlF_3-Al_2O_3$ melts and suspensions were studied both under stationary and non-stationary conditions.

It was shown that the introduction of Al_2O_3 slurry and increases in its proportion in the suspension increases cathode potential (over potential) and decreases the limit current density of aluminum electrowinning under stationary conditions for all investigated temperatures and $[KF]/[AlF_3]$ ratios. The diffusion coefficients of the electroactive ions at the cathode were estimated from the voltammograms. It was shown from both stationary and non-stationary measurements that the introduction of slurred Al_2O_3 into the suspension and increases in its proportion impede the diffusion of the electroactive ions to the cathode.

The parameters for the suspension electrolysis were chosen on the basis of electrochemical measurements. The possibility of producing aluminum through the electrolysis of a $KF-AlF_3-Al_2O_3$ suspension with 45 wt% Al_2O_3 in the solid phase was demonstrated.

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